

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 03 August 2001 (03.08.01)	
<b>International application No.</b> PCT/JP00/07443	<b>Applicant's or agent's file reference</b> H819-PCT
<b>International filing date (day/month/year)</b> 24 October 2000 (24.10.00)	<b>Priority date (day/month/year)</b> 25 October 1999 (25.10.99)
<b>Applicant</b> UCHIDA, Hiroshi et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

02 May 2001 (02.05.01)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland	<b>Authorized officer</b>  Antonia Muller
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

# INTERNATIONAL SEARCH REPORT

Int'l. Application No

PCT/JP 00/07443

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C07C67/04 C07C69/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 562 139 A (SHOWA DENKO KABUSHIKI KAISHA) 29 September 1993 (1993-09-29) page 18 -page 19; claims	1
A	EP 0 757 027 A (BP CHEMICALS LIMITED) 5 February 1997 (1997-02-05) page 20 -page 22; claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*A\* document member of the same patent family

Date of the actual completion of the international search

7 February 2001

Date of mailing of the international search report

16/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Kinzinger, J

# INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/JP 00/07443

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 562139	A	29-09-1993	US 5189201 A	23-02-1993
EP 757027	A	05-02-1997	CA 2182558 A	03-02-1997
			CN 1150585 A	28-05-1997
			DE 69607536 D	11-05-2000
			EP 0959064 A	24-11-1999
			JP 9118647 A	06-05-1997
			SG 49973 A	15-06-1998
			US 5861530 A	19-01-1999

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

10

Applicant's or agent's file reference H819-PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/JP00/07443	International filing date (day/month/year) 24/10/2000	Priority date (day/month/year) 25/10/1999
International Patent Classification (IPC) or national classification and IPC C07C67/04		
Applicant SHOWA DENKO K. K. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.  
☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.



3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

RECEIVED

JUN 24 2002

TECH CENTER 1600/2900

Date of submission of the demand 02/05/2001	Date of completion of this report 03.01.2002
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Cooper, S  Telephone No. +49 89 2399 8323 

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP00/07443

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-29 as originally filed

**Claims, No.:**

1-18 as originally filed

**Drawings, sheets:**

1/3-3/3 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP00/07443

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-18
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

D1: EP-A-0 562 139 (SHOWA DENKO KABUSHIKI KAISHA) 29 September  
1993 (1993-09-29)

**Section V.**

- 1). The present application relates to a process for preparing an ethyl ester by acid catalysed reaction between ethylene and a carboxylic acid. The process is novel over the process disclosed in D1 because it specifies that the ethylene starting material should contain less than a certain value of higher olefins. Where ethylene is the starting material in the process of D1, no value for its content of other olefins is given.
- 2). The present invention is said to reside in the recognition that the space time yield of ethyl ester decreases and the level of impurity increases if the amount of olefins other than ethylene or compounds capable of giving rise to such olefins other than ethylene under reaction conditions exceeds specified values.
- 3). From D1, p.2, lines 45 et seq it is known that olefins other than ethylene are capable of reacting with carboxylic acids under the present reaction conditions. It is therefore not surprising that if such olefins are present in the reaction of ethylene and a carboxylic acid they will compete with the ethylene for the carboxylic acid to produce compounds other than the ethyl ester, thus increasing the level of impurities in the ethyl ester and reducing its space time yield. The process of the present claims is therefore not inventive.

# PATENT COOPERATION TREATY

## PCT

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### INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>H819-PCT</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/JP 00/ 07443</b>	International filing date (day/month/year) <b>24/10/2000</b>	(Earliest) Priority Date (day/month/year) <b>25/10/1999</b>
Applicant  <b>SHOWA DENKO K. K. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/07443

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/04 C07C69/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 562 139 A (SHOWA DENKO KABUSHIKI KAISHA) 29 September 1993 (1993-09-29) page 18 -page 19; claims ---	1
A	EP 0 757 027 A (BP CHEMICALS LIMITED) 5 February 1997 (1997-02-05) page 20 -page 22; claims -----	1

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

7 February 2001

Date of mailing of the international search report

16/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Kinzinger, J

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 00/07443

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 562139	A	29-09-1993	US	5189201 A	23-02-1993
EP 757027	A	05-02-1997	CA	2182558 A	03-02-1997
			CN	1150585 A	28-05-1997
			DE	69607536 D	11-05-2000
			EP	0959064 A	24-11-1999
			JP	9118647 A	06-05-1997
			SG	49973 A	15-06-1998
			US	5861530 A	19-01-1999



## PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

To:

A. AOKI, ISHIDA, & ASSOCIATES  
Attn. ISHIDA, Takashi  
Toranomon 37 Mori Bldg., 5-1,  
Toranomon 3-chome, Minato-Ku  
TOKYO 105-8423  
JAPAN



(PCT Rule 44.1)

77

Date of mailing  
(day/month/year)

16/02/2001

Applicant's or agent's file reference

H819-PCT

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/JP 00/07443

International filing date

(day/month/year)

24/10/2000

Applicant

SHOWA DENKO K. K. et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Fascimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Ralf Ockers

## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

#### What documents must/may accompany the amendments?

##### Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

### "Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

### Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

### Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>H819-PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/JP 00/07443</b>	International filing date (day/month/year) <b>24/10/2000</b>	(Earliest) Priority Date (day/month/year) <b>25/10/1999</b>
Applicant  <b>SHOWA DENKO K. K. et al.</b>		

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☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

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2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

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☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

National Application No

PCT/JP 00/07443

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C67/04 C07C69/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 562 139 A (SHOWA DENKO KABUSHIKI KAISHA) 29 September 1993 (1993-09-29) page 18 -page 19; claims ---	1
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☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR PRODUCING ESTERS

(57) Abstract: A process for producing an ester comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the concentration of olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene. The deterioration of the catalyst can be remarkably prevented from proceeding and a continuous and stable operation can be performed for a long time.

WO 01/30738 A1

## DESCRIPTION

PROCESS FOR PRODUCING ESTERS

Cross-Reference to related Applications

5        This application is an application filed under  
35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C.  
§119(e)(1) of the filing date of the Provisional  
Application 60/192,880 filed March 29, 2000, pursuant to  
35 U.S.C. §111(b).

10       Technical Field

The present invention relates to a process for  
producing an ester by reacting an ethylene and a  
carboxylic acid.

Background Art

15       It is well known that a lower olefin and a lower  
aliphatic carboxylic acid react in the presence of an  
acid catalyst to provide the corresponding ester. It is  
also known that in this reaction, a heteropolyacid and/or  
heteopolyacid salt effectively act as a catalyst.

20       Specific examples of these conventional techniques  
include those described, for example, in Japanese  
Unexamined Patent Publications No. 4-139148, No. 4-  
139149, No. 5-65248, No. 5-163200, No. 5-170699, No. 5-  
255185, No. 5-294894, No. 6-72951 and No. 9-118647.

25       Thus, the development of catalysts having high initial  
activities is proceeding.

However, in industrial production processes,  
impurities derived from the starting materials or by-  
products produced during the reaction cause deterioration  
30       of the catalyst and in turn the reaction yield  
disadvantageously decreases. Particularly, in the  
process having a circulation system, if a reaction is  
continuously performed for a long time, various  
impurities or by-products accumulate in the system and  
35       due to the effect thereof, for example, a vicious circle  
arises such that the catalyst deteriorates and the side  
reaction is further accelerated.

## Disclosure of Invention

It is an object of the present invention to provide a process for producing an ester by esterifying a carboxylic acid with ethylene in a vapor phase, where the operation can be continuously and stably performed for a long period of time.

In particular, the object of the present invention is to provide the above-described process for producing an ester where, in a process having a circulation system, the impurities derived from the starting materials or the compounds derived from the by-products produced by a side reaction are reduced to a low concentration with respect to the starting materials, so that the catalyst can be prevented from deteriorating and, in turn, the operation can be continuously and stably performed for a long period of time.

The present inventors have made extensive studies to investigate a process for producing an ester, by reacting ethylene and a carboxylic acid, in which deterioration of the catalyst hardly occurs and the operation can be continuously and stably performed over a long period of time.

As a result, it has been found that, in a process for producing an ester by esterifying a carboxylic acid and an ethylene using an acid catalyst in a vapor phase, when the concentration of olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene, the deterioration of the catalyst can be remarkably prevented from proceeding and in turn, a continuous and stable operation can be performed for a long time.

It has also been found that, in the process for producing an ester by esterifying a carboxylic acid and ethylene using an acid catalyst in a vapor phase, when the concentration of olefin equivalent in the starting materials is controlled to 50,000 ppm or less in terms of

the molar ratio to the total of the olefin equivalent and ethylene, the deterioration of the catalyst can be remarkably prevented from proceeding and a continuous and stable operation can be performed for a long time, as in the above-mentioned process.

#### Brief Description of Drawings

Fig. 1 is a schematic view showing a one-path process according to the invention having no circulation step, wherein acetic acid is used as a carboxylic acid.

Fig. 2 is a schematic view showing a process according to the invention having a circulation step from subsequent step, wherein acetic acid is used as a carboxylic acid.

Fig. 3 is a schematic view of a testing apparatus used in the examples.

#### Best Mode for Carrying Out the Invention

The present invention is described in detail below.

The term "olefin having 3 or more carbon atoms" as used herein generally refers to one or more olefins except for ethylene. Specific examples thereof include linear terminal olefins having 3 or more carbon atoms, such as propylene, 1-butene, 2-butene, isobutene, 1-hexene and 2-octene, internal olefins, branched terminal olefins, branched internal olefins, and cyclic olefins having 3 or more carbon atoms, such as cyclopentene and cyclohexene.

Among these, so-called ethylene oligomers derived from an ethylene and produced by the side reaction which may occur under the esterification reaction conditions, such as 1-butene, cis-2-butene, trans-2-butene, 2-methyl-2-pentene and 3-methyl-2-pentene, have a possibility of causing a problem. Of course, the olefins are not limited thereto.

The term "olefin equivalent" as used herein refers to one or more compounds which can produce the olefin having 3 or more carbon atoms under the esterification reaction conditions. Specific examples thereof include

hydrates of olefins having 3 or more carbon atoms, ether compounds produced by the reaction of the hydrate with ethylene or an olefin having 3 or more carbon atoms, and carboxylic acid esters produced by the reaction of a carboxylic acid with an olefin having 3 or more carbon atoms. However, the olefin equivalent is not limited thereto and all compounds are included as long as they are compounds capable of producing an olefin having 3 or more carbon atoms under the esterification reaction conditions.

Specific examples of the olefin equivalent include the following compounds.

Examples of the hydrate of an olefin having 3 or more carbon atoms include isopropanol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol and 2-hexanol.

Examples of the ether compound produced by the reaction of a hydrate of an olefin having 3 or more carbon atoms with ethylene or an olefin having 3 or more carbon atoms include ethyl isopropyl ether, ethyl sec-butyl ether, ethyl t-butyl ether, di-sec-butyl ether, di-n-butyl ether and ethyl cyclohexyl ether.

Examples of the carboxylic acid ester produced by the reaction of a carboxylic acid with an olefin having 3 or more carbon atoms include isopropyl acetate, sec-butyl acetate, sec-butyl propionate, t-butyl acetate and cyclohexyl acetate.

These compounds, namely, hydrates of olefins, ether compounds and carboxylic acid esters, are the specific examples of the equivalent of an olefin. However, needless to say, the specific examples of the olefin equivalent is not limited thereto.

The olefin equivalent also includes those produced in the reaction system as well as those contained in the starting materials newly fed to the reaction system.

Particularly, in performing the process for producing an ester by the esterification reaction of a carboxylic acid and ethylene using an acid catalyst in a

vapor phase, when water is present in the system, there is a possibility that a hydrate may be produced by the hydration of ethylene and also an ether compound or a carboxylic acid ester is further produced from the hydrate. Furthermore, when a circulation system for the unreacted raw materials is integrated into the production process of an ester so as to improve the yield or the like, the hydrate, the ether compound and the carboxylic acid ester produced in the reaction system may disadvantageously mingle with the unreacted starting materials. In this document, the "olefin equivalent" as used herein includes the hydrates, ether compounds and carboxylic acid esters produced in the reaction system by the esterification reaction.

In the process for producing an ester according to the present invention, the concentration of olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene, which is effective in reducing the deterioration rate of the catalyst and in turn continuously and stably performing the operation for a long period of time.

The terms "the concentration of olefin having 3 or more carbon atoms in the starting materials" and "the concentration of olefin equivalent in the starting materials" each refers to a concentration immediately before the inlet of a reactor for performing the esterification reaction.

For example, specifically, in the case where the reaction is performed in the one-path process having no circulation step as shown in Fig. 1, the concentration immediately before the inlet of a reactor indicated by (1) applies. In the process having a circulation step from a subsequent step as shown in Fig. 2, the concentration immediately before the inlet of a reactor indicated by (2) applies. Needless to say, the present invention is by no means limited to these exemplified

processes.

Accordingly, the term "starting materials" as used herein of course includes those obtained by recovering unreacted starting materials, through a subsequent step  
5 such as separation of the objective compound, after the reaction and supplied to the reactor via a circulation system, in addition to ethylene and acetic acid newly fed to the reaction system.

The position (1) in the process shown in Fig. 1 and  
10 the position (2) in the process shown in Fig. 2 are both kept at a temperature equal to or higher than the reaction temperature in the reactor. Accordingly, to measure the concentration at such a position, the sampling must be particularly designed.

15 In particular, some olefin equivalents are readily condensed when cooled to room temperature and, therefore, to avoid measurement errors due to the effect thereof, the sampling must be designed, for example, to separate the condensed components from the non-condensed  
20 components by cooling them using an ice trap or the like and analyze respective components.

If the concentration of olefin having 3 or more carbon atoms in the starting materials exceeds 10,000 ppm in terms of the molar ratio to the total of the olefin  
25 and ethylene, the catalytic activity decreases at an extremely high rate and, as a result, the catalyst life is greatly shortened. This is thought to occur because the above-described olefin reacts with ethylene on the catalyst to produce cokes and the active sites of the  
30 catalyst are covered by the cokes to cause the deactivation.

Accordingly, the concentration of olefin having 3 or more carbon atoms in the starting materials is preferably as low as possible. These olefins cannot be completely  
35 removed with ease, but the concentration is preferably 5,000 ppm or less, more preferably 1,000 ppm or less.

The method for controlling the concentration of

olefin having 3 or more carbon atoms in the starting materials to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene is not particularly limited. Commonly known separation techniques may be used.

As an example, fundamentally, ethylene used as a starting material should of course be refined to reduce the contents of these compounds as much as possible.

The olefin having 3 or more carbon atoms produced by the side reaction within the reaction system, which becomes a problem when a circulation system is integrated, can be separated from the ethylene by a method of allowing an appropriate solvent to absorb the main products exclusive of the ethylene, the starting materials and the by-products in the reaction gas discharged from the reactor. Also, the raw material gas may be separated from ethylene by high-pressure or low-temperature distillation or by using a separation membrane or the like. Other than these specific examples, any method may be used as long as it is a method capable of controlling the concentration of the olefin having 3 or more carbon atoms circulated and guided to the reactor to 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

If the concentration of olefin equivalent in the starting materials exceeds 50,000 ppm in terms of the molar ratio to the total of the olefin equivalent and ethylene, similarly to the case where the concentration of olefin having 3 or more carbon atoms exceeds 10,000 ppm in terms of the molar ratio to the total of the olefin and ethylene, the catalytic activity decreases at an extremely high rate and, as a result, the catalyst life is greatly shortened.

Although it may slightly differ depending on the individual olefin equivalents, the olefin equivalent generally exhibits an activity of deteriorating the catalyst on the same level as the olefin having 3 or more



carbon atoms when the concentration thereof is about 5 times higher. This difference is considered to result from the fact that the olefin equivalent produces an olefin after being decomposed on the catalyst and, therefore, the effect on the deactivation is low even if the concentration is higher than that of the olefin.

However, similarly to the olefin having 3 or more carbon atoms, the concentration of the olefin equivalent is preferably as low as possible. Although complete removal of the olefin equivalent may not be attained with ease, the concentration thereof is preferably 25,000 ppm or less, more preferably 5000 ppm or less.

The method for controlling the concentration of olefin equivalent in the starting materials to 50,000 ppm or less in terms of a molar ratio to the total of the olefin equivalent and ethylene is not particularly limited. Similarly to the olefin having 3 or more carbon atoms, commonly known separation techniques may be used for the olefin equivalent.

When the olefin having 3 or more carbon atoms and the olefin equivalent are present together, an interaction therebetween is not particularly observed. Roughly, the sum of one-fifth the concentration of all olefin equivalents and the concentration of olefin having 3 or more carbon atoms in the starting materials is preferably 10,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

Needless to say, similarly to their individual concentrations, the concentration here is also preferably as low as possible and, specifically, it is preferably 5,000 ppm or less, more preferably 1,000 ppm or less.

The method for measuring the concentration of the olefin having 3 or more carbon atoms or the olefin equivalent is not particularly limited and any method may be used as long as it is a method commonly used for measuring the concentration. Specific examples of the

measuring method include a method of placing a cell in a part of the apparatus and spectro-optically measuring the concentration using an appropriate wavelength, and a method of sampling a part of the starting material and  
5 analyzing it by gas chromatography. However, the present invention is by no means limited thereto.

The optimal measuring method varies depending on the properties of the object to be measured or the environment of the measurement, but a method which is  
10 free of any effect from other components is favored with good quantitation and reproduction, is low in measuring threshold value, and is simple and inexpensive, is preferred.

The carboxylic acid for use as a reaction starting material in the present invention is a lower aliphatic carboxylic acid having from 1 to 4 carbon atoms.  
15 Preferred are formic acid, acetic acid, acrylic acid, propionic acid and methacrylic acid, and more preferred are acetic acid and acrylic acid.

The acid catalyst for use in the present invention is a compound widely used as an acid catalyst such as ion-exchange resin, mineral acid, heteropolyacid, zeolite and composite metal oxide. Preferred are a  
20 heteropolyacid and a heteropolyacid salt. A heteropolyacid is a compound consisting of a center element and peripheral elements to which oxygen is bonded.  
25

The center element is usually silicon or phosphorus but not limited thereto and the center element may be any one selected from the elements belonging to Groups 1 to  
30 17 of the Periodic Table. The Periodic Table as used herein indicates the Periodic Table provided in Muki Kagaku Meimeiho, Kaitei-Ban (Nomenclature in Inorganic Chemistry, Revised), Kokusai Junsei Oyobi Oyo Kagaku Rengo (1989).

35 Specific examples of the center element include cupric ion; divalent beryllium, zinc, cobalt and nickel ions; trivalent boron, aluminum, gallium, iron, cerium,

arsenic, antimony, phosphorus, bismuth, chromium and rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulfur, tellurium, manganese, nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium and antimony ions; hexavalent tellurium ion; and heptavalent iodide ion, but the present invention is by no means limited thereto.

Specific examples of the peripheral element include tungsten, molybdenum, vanadium, niobium and tantalum, but the present invention is not limited thereto.

These heteropolyacids are also known, e.g., as "polyoxoanion", "polyoxometallate" or "metal oxide cluster". The structures of some of the well known anions are known, for example, as Keggin, Wells-Dawson or Anderson-Evans-Perloff structures. Heteropolyacids usually have a high molecular weight, for example, a molecular weight, e.g., in the range of 700 to 8,500 and include dimeric complexes.

The heteropolyacid salt is not particularly limited as long as it is a metal salt or onium salt resulting from substituting a part or all of the hydrogen atoms of the heteropolyacid.

Specific examples thereof include metal salts, e.g., such as of lithium, sodium, potassium, cesium, magnesium, barium, copper, gold and gallium, and onium salts such as of ammonia, but the present invention is not limited thereto.

Particularly when the heteropolyacid is in a free acid form or in a certain salt form, the heteropolyacid has a relatively high solubility in polar solvents such as water or other oxygenated solvents, and the solubility can be controlled by selecting the appropriate counter ions.

Examples of the heteropolyacid which can be particularly preferably used as a catalyst in the present invention include:

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMo_{12}O_{40}] \cdot xH_2O$
Molybdosilicic acid	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstosilicic acid	$H_{4+n}[SiMo_nW_{12-n}O_{40}] \cdot xH_2O$
Molybdotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$

wherein n is an integer of 1 to 11 and x is an integer of at least 1.

Particularly preferred examples of the heteropolyacid salt include lithium salts, sodium salts, 5 potassium salts, cesium salts, magnesium salts, barium salts, copper salts, gold salts, gallium salts and ammonium salts of the above-described heteropolyacids which are particularly preferred.

The acid catalyst may be supported on a support. In 10 this case, the acid catalyst content is preferably from 10 to 200 mass%, more preferably from 50 to 150 mass%, based on the entire mass of the support.

If the acid catalyst content is less than 10 mass%, the content of active components in the catalyst may 15 excessively be lower and the activity per the catalyst unit mass may disadvantageously decrease.

If the content of the acid catalyst exceeds 200 mass%, the effective surface area may decrease and, as a result, the effect owing to the increase in the supported

amount may not be brought out and at the same time, coking is disadvantageously liable to occur to greatly shorten the catalyst life.

5       The substance which can be used as a support for the acid catalyst of the present invention is not particularly limited and those capable of providing, when prepared as a catalyst by carrying the acid catalyst, a catalyst having a specific surface area of from 65 to 350 m<sup>2</sup>/g, as measured by BET method, is preferred.

10       The shape of the substance which can be used as a support for the catalyst of the present invention is not particularly limited and, specifically, a powder, spheres, pellets and any other forms may be used. Specific examples thereof include silica, diatomaceous  
15       earth, montmorillonite, titania, activated carbon, alumina and silica-alumina, but the present invention is not limited thereto.

20       The support is preferably a support comprising a siliceous main component and having a spherical or pellet shape, more preferably a silica having a purity of 95 mass% or more based on the entire mass of the support.

25       The average diameter thereof is preferably from 2 to 10 mm for use in a fixed bed system and from powder to 5 mm for use in a fluid bed system, though it varies depending on the reaction form.

30       The acid catalyst for use in the present invention can be produced by any desired method. For example, a process for preparing a heteropolyacid and/or heteropolyacid salt catalyst is described below, which comprises first and second steps.

First Step:

A step for obtaining a solution or suspension of a heteropolyacid and/or a heteropolyacid salt.

Second Step:

35       A step for supporting the solution or suspension obtained in the first step on a support.

The solvent which can be used in the first step is

not particularly limited as long as it can uniformly dissolve or suspend the desired heteropolyacid and/or heteropolyacid salt, and water, an organic solvent or a mixture thereof may be used. Preferred examples thereof  
5 include water, alcohols and carboxylic acids, but the present invention is not limited thereto.

The method for dissolving or suspending a heteropolyacid and/or a heteropolyacid salt in the solvent is not particularly limited and any method may be  
10 used as long as it can uniformly dissolve or suspend a desired heteropolyacid and/or heteropolyacid salt.

For example, in the case of a heteropolyacid, namely, a free acid, if it can dissolve, the heteropolyacid may be dissolved as it is. Even when the  
15 heteropolyacid cannot completely dissolve, if the heteropolyacid can be uniformly suspended by forming it into fine powder, the heteropolyacid may be suspended as such. In the case of a heteropolyacid salt, a method of dissolving a heteropolyacid and a starting material salt  
20 for a neutralizing element together or separately and then mixing them to prepare a uniform solution or suspension may be used. Furthermore, in the case of a compound which is in the state of a heteropolyacid salt, a uniform solution or suspension may be obtained in the  
25 same manner as in the heteropolyacid.

The optimal volume of the solution or suspension varies depending on the supporting method in the second step and the support used but this is not particularly limited.

30 The second step is a step for supporting a solution or suspension of a heteropolyacid and/or a heteropolyacid salt obtained in the first step on a support to obtain a catalyst for use in the manufacture of a lower aliphatic ester.

35 The method for bearing the solution or suspension of a heteropolyacid and/or a heteropolyacid salt on a support is not particularly limited and a known method

may be used.

For example, the catalyst may be prepared by dissolving or suspending a heteropolyacid and/or a heteropolyacid salt in a solvent so as to form a solution or suspension corresponding to the liquid absorption  
5 amount of the support and impregnating a support with the solution or suspension.

The catalyst may also be prepared by using an excess solution or suspension, impregnating it into a support  
10 while moderately moving the support in the solution or suspension of a heteropolyacid and/or a heteropolyacid salt and then removing the excess acid through filtration.

The wet catalyst obtained as such is preferably dried by placing it in a heating oven for a few hours.  
15 Thereafter, the catalyst is cooled to the ambient temperature in a desiccator. The drying temperature is not particularly limited but if it exceeds about 400°C, the skeleton of the heteropolyacid may be  
20 disadvantageously destroyed. The drying temperature is preferably from 80 to 350°C.

Industrially, the catalyst may be continuously dried using a dryer such as through-flow rotary dryer, continuous fluidized bed dryer or continuous hot air  
25 carrier type dryer.

The amount of the heteropolyacid and/or heteropolyacid salt supported can be calculated simply by subtracting the mass of the support used from the dry mass of the catalyst prepared. A more exact amount may  
30 be measured by chemical analysis such as ICP (inductively coupled plasma emission spectrometry).

In practicing the process for producing an ester of the present invention, the ratio between ethylene and the carboxylic acid used is preferably such that ethylene is  
35 used in an equimolar amount or excess molar amount to the carboxylic acid. The ratio of ethylene : carboxylic acid is preferably, as a molar ratio, from 1:1 to 30:1, more

preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

5 In the process of the present invention, the vapor phase reaction may be performed in either a fixed bed system or a fluidized bed system. The shape of the support may also be selected from those formed into a size of from powder to a few mm in diameter according to the system of the practice.

10 In the process of the present invention, a slight amount of water is preferably mixed in the starting materials from the standpoint of the catalyst life. However, if an excessively large amount of water is added, by-products such as alcohol and ether may disadvantageously increase. In general, the amount of  
15 water is preferably from 1 to 15 mol%, more preferably from 2 to 8 mol%, in the entire amount of the olefin and carboxylic acid used.

The reaction temperature and pressure must be in the range capable of keeping the supply medium in a gaseous form and varies depending on the starting materials used.  
20 In general, the reaction temperature is preferably from 120 to 250°C, more preferably from 140 to 220°C.

The pressure is preferably from atmospheric pressure to 3 MPa, more preferably from atmospheric pressure to 2  
25 MPa.

With respect to the space velocity (GHSV) of the raw materials, these preferably pass through the catalyst layer at a GHSV of from 100 to 7,000/hr, more preferably from 300 to 3,000/hr.

30 The present invention is further illustrated below by referring to the examples and reference examples. However, these examples are only for describing the embodiments of the present invention, and the present invention should not be construed as being limited  
35 thereto.

#### Analysis of Reaction Gas

In Examples 1 to 12 and Comparative Examples 1 to 7



which are examples of the one-path process having no recycle system, the starting material composition fed to the reactor was used as the inlet gas concentration.

5 In Examples 13 to 15 and Comparative Example 8 which are examples of the process having a recycle system, for a gas at the inlet of the reactor, when a predetermined time was passed after the initiation of the reaction, a part of the gas was sampled by a three-way valve and cooled and the concentrated solution collected was  
10 recovered in the whole amount and analyzed by gas chromatography. With respect to the effluent gas remaining uncondensed, the flow rate of the gas at the outlet discharged within the sampling time was measured and a part of the gas was sampled and analyzed on the  
15 composition by gas chromatography. On the other hand, for a gas at the outlet, the whole amount of the gas was cooled and the concentrated reaction solution collected was recovered in the whole amount and analyzed by gas chromatography. With respect to the effluent gas  
20 remaining uncondensed, the flow rate of the gas at the outlet discharged within the sampling time was measured and a part of the gas was sampled and analyzed on the composition by gas chromatography. The analysis conditions are shown below.

25 Conditions for Analysis of Uncondensed Gas

An absolute calibration curve method was used for the analysis. The analysis was performed under the following conditions by sampling 50 ml of the effluent gas and allowing the whole amount thereof to flow into a  
30 1 ml-volume gas sampler attached to the gas chromatograph.

1. Ether, Carboxylic Acid Ester, Alcohol, Trace By-Products

Gas chromatography:

35 gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu gas chromatograph

## Column:

packed column SPAN80 15% Shinchrom A, 60 to 80 mesh  
(length: 5 m)

## Carrier gas:

5 nitrogen (flow rate: 25 ml/min)

## Temperature conditions:

constant temperature conditions where the detector  
and the vaporization chamber were at 120°C and the  
column was at 65°C

## 10 Detector:

FID (H<sub>2</sub> pressure: 60 kPa, air pressure: 100 kPa)

## 2. Butene

## Gas chromatography:

15 gas chromatograph (GC-14B, manufactured by Shimadzu  
Corporation) with a gas sampler (MGS-4, measuring  
tube: 1 ml) for Shimadzu gas chromatograph

## Column:

packed column Unicarbon A-400, length: 2 m

## Carrier gas:

20 helium (flow rate: 23 ml/min)

## Temperature conditions:

the temperatures of the detector and the  
vaporization chamber were 120°C and the column  
temperature was elevated from 40°C to 95°C at a  
25 temperature increasing rate of 40°C/min

## Detector:

FID (H<sub>2</sub> pressure: 70 kPa, air pressure: 100 kPa)

## 3. Ethylene

## Gas chromatography:

30 gas chromatograph (GC-14B, manufactured by Shimadzu  
Corporation) with a gas sampler (MGS-4, measuring  
tube: 1 ml) for Shimadzu gas chromatograph

## Column:

packed column Unibeads 1S, length: 3 m

## 35 Carrier gas:

helium (flow rate: 20 ml/min)

Temperature conditions:

constant temperature conditions where the detector and the vaporization chamber were at 120°C and the column was at 65°C

5 Detector:

TCD (He pressure: 70 kPa, current: 90 mA, temperature: 120°C)

Analysis of Collected Solution

10 The analysis was performed using the internal standard method, where the analysis solution was prepared by adding 1 ml of 1,4-dioxane as the internal standard to 10 ml of the reaction solution and 0.4 µl of the analysis solution was injected.

Gas chromatography:

15 GC-14B, manufactured by Shimadzu Corporation

Column:

capillary column TC-WAX (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm)

Carrier gas:

20 nitrogen (split ratio: 20, column flow rate: 2 ml/min)

Temperature conditions:

25 the temperatures of the detector and the vaporization chamber were both 200°C and the column was kept at 50°C for 5 minutes from the initiation of the analysis, thereafter rising to 150°C at a temperature increasing rate of 20°C/min, and kept at 150°C for 10 minutes

Detector:

30 FID (H<sub>2</sub> pressure: 70 kPa, air pressure: 100 kPa)  
Support

Support 1:

35 natural silica (KA-0, produced by SUD-CHEMIE AG)  
(specific surface area: 68.5 m<sup>2</sup>/g, pore volume: 0.71 cm<sup>3</sup>/g)

## Support 2:

synthetic silica (CARiACT Q-10, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 219.8 m<sup>2</sup>/g, pore volume: 0.660 cm<sup>3</sup>/g)

## 5 Support 3:

natural silica (KA-1, produced by SUD-CHEMIE AG) (specific surface area: 113 m<sup>2</sup>/g, pore volume: 0.64 cm<sup>3</sup>/g)

## Support 4:

10 natural silica (KA-160, produced by SUD-CHEMIE AG) (specific surface area: 130 m<sup>2</sup>/g, pore volume: 0.53 cm<sup>3</sup>/g)

## Support 5:

15 synthetic silica (CARiACT Q-6, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 450 m<sup>2</sup>/g, pore volume: 0.6 cm<sup>3</sup>/g)

## Support 6:

20 synthetic silica (CARiACT Q-15, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 200 m<sup>2</sup>/g, pore volume: 1.0 cm<sup>3</sup>/g)

## Support 7:

synthetic silica (CARiACT Q-30, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 100 m<sup>2</sup>/g, pore volume: 1.0 cm<sup>3</sup>/g)

## 25 Support 8:

synthetic silica (N-602A, produced by Nikki Kagaku K.K.) (specific surface area: 290 m<sup>2</sup>/g, pore volume: 0.8 cm<sup>3</sup>/g)

## Support 9:

30 synthetic silica (N-601A3, produced by Nikki Kagaku K.K.) (specific surface area: 264 m<sup>2</sup>/g, pore volume: 0.9 cm<sup>3</sup>/g)

## Support 10:

35 synthetic silica (N-602T, produced by Nikki Kagaku K.K.) (specific surface area: 132 m<sup>2</sup>/g, pore volume: 0.7 cm<sup>3</sup>/g)

## Preparation Process of Catalyst 1

The support 1 was dried for 4 hours in a (hot air) dryer previously adjusted to 110°C. 1 L of the previously dried carrier was subjected to the measurement of the bulk density by a 1 L-volume messcylinder. Tungstophosphoric acid and lithium nitrated were added each to the weight shown in Table 1, 15 ml of pure water was added thereto, and the mixture was uniformly dissolved to obtain a  $\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  aqueous solution (impregnating solution). This impregnating solution was charged into the messcylinder and pure water was added to reach the liquid amount shown in the amount of prepared solution in Table 1 and then uniformly stirred. The previously dried support was weighed to the amount described in Table 1, added to the impregnating solution and thoroughly stirred, thereby impregnating the support. The support impregnated with the solution was air dried for 1 hour and thereafter dried for 5 hours by a hot air dryer adjusted to 150°C. The weight of the catalyst obtained was measured.

## Preparation Process of Catalysts 2 to 12

The preparation was performed as described in Preparation Process of Catalyst 1 by changing the kind and weight of the support, the kind and weight of the catalyst component and the weight of lithium nitrate as shown in Table 1. The catalyst was supported on the support in the same manner as in Preparation Process of Catalyst 1.

Table 1

Name of Catalyst	Support	Bulk Density (g/L)	Weight of Support (g)	Kind of Catalyst Component	Amount of Catalyst Component (g)	Amount of Lithium Nitrate (g)	Volume of Prepared Solution (ml)	Dry Weight (g)
catalyst 1	1	558	55.8	HPW	65.33	0.1318	34	113.6
catalyst 2	2	456	45.6	HSiW	34.88	0.0719	43	75.6
catalyst 3	3	573	57.3	HPW	65.33	0.1318	33	124.5
catalyst 4	4	575	57.5	HPW	65.33	0.1318	32	113.8
catalyst 5	5	627	62.7	HSiW	34.88	0.0719	33	94.3
catalyst 6	6	446	44.6	HSiW	34.88	0.0719	40	75.2
catalyst 7	7	432	43.2	HSiW	34.88	0.0719	41	74.5
catalyst 8	8	811	81.1	HPW	35.63	0.0718	64	114.7
catalyst 9	9	703	70.3	HPW	35.63	0.0718	83	102.9
catalyst 10	10	813	81.3	HPW	35.63	0.0718	69	114.3
catalyst 11	2	456	45.6	HPVW	35.90	0.0753	43	76.3
catalyst 12	2	456	45.6	HSiVW	35.90	0.0753	43	75.9

HPW:  $H_3PW_{12}O_{40}$   
 HSiW:  $H_4SiW_{12}O_{40}$   
 HPVW:  $H_4PVW_{12}O_{40}$   
 HSiVW:  $H_5SiVW_{12}O_{40}$

## Example 1

40 ml of the catalyst obtained by Preparation Process of Catalyst 1 was filled in a reaction tube and a mixed gas of ethylene : acetic acid : steam : nitrogen  
5 shown in Table 2 was introduced therein at a temperature of 165°C and a pressure of 0.8 MPaG (gauge pressure) to perform the reaction. The results are shown in Table 3.

Table 2

	Catalyst	Starting Material Gas, ethylene:acetic acid: water:nitrogen: substance added (molar ratio)	Substance Added (ppm) *1	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Reaction Time (hr)	Reaction Temperature (°C)
Example 1	1	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 2	2	78.5:8.0:4.5:9.0	none	60.0	0.8	5 99	165
Example 3	3	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 4	4	78.5:8.0:4.5:9.0	none	60.0	0.8	5 103	165
Example 5	5	78.5:8.0:4.5:9.0	none	60.0	0.8	5 98	165
Example 6	6	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 7	7	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 8	8	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 9	9	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 10	10	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 11	11	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 12	12	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Comparative Example 1	1	78.5:8.0:4.5:8.2:0.8	1-butene (10088)	60.5	0.8	5 100	165



Table 2 (continued)

	Catalyst	Starting Material Gas, ethylene:acetic acid: water:nitrogen: substance added (molar ratio)	Substance Added (ppm) *1	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Reaction Time (hr)	Reaction Temperature (°C)
Comparative Example 2	1	78.5:8.0:4.5:8.2:0.8	2-octene (10088)	60.5	0.8	5	165
						103	
Comparative Example 3	1	78.5:8.0:4.5:8.2:0.8	TMP (10088)	60.5	0.8	5	165
						98	
Comparative Example 4	2	78.5:8.0:4.5:8.2:0.8	1-butene (19975)	60.5	0.8	5	165
						102	
Comparative Example 5	1	78.5:8.0:4.5:7.4:1.6	2-BA (19975)	61.0	0.8	5	165
						105	
Comparative Example 6	1	78.5:8.0:4.5:8.2:0.8	2-BuOH (19975)	61.0	0.8	5	165
						98	
Comparative Example 7	2	78.5:8.0:4.5:7.8:1.2	2-BEE (15056)	60.7	0.8	5	165
						100	

TMP: 2,2,4-trimethylolpentane  
 2-BEE: 2-butyl ethyl ether  
 2-BA: 2-butyl acetate  
 2-BuOH: 2-butyl alcohol  
 \*1: concentration (ppm) when additive/(ethylene + substance added)

Table 3

	Catalyst	Substance Added (ppm)*1	STY of Ethyl Acetate (g/L- hr)	Trace By- Products (wt%)
Example 1	1	none	191	0.0047
			186	0.0123
Example 2	2	none	252	0.0001
			236	0.0007
Example 3	3	none	212	0.0004
			204	0.0160
Example 4	4	none	224	0.0127
			213	0.0234
Example 5	5	none	268	0.0003
			251	0.0010
Example 6	6	none	189	0.0003
			180	0.0005
Example 7	7	none	130	0.0004
			125	0.0008
Example 8	8	none	178	0.0009
			169	0.0012
Example 9	9	none	95	0.0006
			90	0.0010
Example 10	10	none	205	0.0303
			185	0.0011
Example 11	11	none	148	0.0303
			140	0.0400
Example 12	12	none	139	0.0160
			131	0.0250

\*1: concentration (ppm) when additive/(ethylene + substance added)

5 Examples 2 to 12

The reactions were performed in the same manner as in Example 1 except for changing Catalyst 1 in Example 1 to Catalysts 2 to 12 as shown in Table 2. The results are shown in Table 3.

10 Comparative Examples 1, 2, 3, 5 and 6

The reactions were performed in the same manner as

in Example 1 except for changing the reaction gas composition as shown in Table 2. The results are shown in Table 4. As compared with Example 1, the STY of ethyl acetate after about 100 hours seriously decreased, trace by-products increased and a part was separated from the reaction solution and became oily.

Table 4

	Catalyst	Substance Added (ppm) *1	STY of Ethyl Acetate (g/L-hr)	Trace By-Products (wt%)
Comparative Example 1	1	1-butene (10088)	200	2.4277
			166	5.3126
Comparative Example 2	1	2-octene (10088)	66	Oil was produced.
			43	Oil was produced.
Comparative Example 3	1	TMP (10088)	197	Oil was produced.
			171	Oil was produced.
Comparative Example 4	2	1-butene (19975)	203	6.3111
			165	8.2766
Comparative Example 5	1	2-BA (19975)	192	1.9833
			153	3.5211
Comparative Example 6	1	2-BuOH (19975)	195	1.5633
			177	3.0122
Comparative Example 7	2	2-BEE (15056)	203	6.3111
			181	7.2812

TMP: 2,2,4-trimethylolpentane

2-BEE: 2-butyl ethyl ether

2-BA: 2-butyl acetate

2-BuOH: 2-butyl alcohol

\*1: concentration (ppm) when additive/(ethylene + substance added)

## Comparative Examples 4 and 7

5 The reactions were performed in the same manner as in Example 2 except for changing the reaction gas composition as shown in Table 2. The results are shown in Table 4. As compared with Example 2, the STY of ethyl acetate seriously decreased and trace by-products increased.

## Example 13

10 750 ml of the catalyst shown in Table 5 was filled in a reactor of a reaction apparatus schematically shown in Fig. 3. The conditions were set such that the temperature of the reactor was 160°C, the temperature of the vaporizer was 180°C, the pressure of the entire system was 0.8 MPaG (gauge pressure) and the condensation  
15 temperature in the scrubber was -5°C. The amount of ethylene fed in Fig. 3 was 49.0 g/hr and the gas not condensed in the scrubber was recycled by a compressor. Other conditions are shown in Table 5.

Table 5

	Catalyst	Gas Composition in (1) after the reaction for 100 Hours, ethylene:acetic acid:water:nitrogen:ethyl acetate:butene (molar ratio)	Butene Concen- tration (ppm)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temper- ature of Scrubber (°C)	Reaction Time (hr)	Reaction Temper- ature (°C)	STY of Ethyl Acetate (g/L-hr)	Trace By- Products (wt%)
Example 13	1	78.5:8.0:4.5:8.8:0.2:0.0016	20	1125	0.8	-5	100	165	181	0.0056
							500		183	0.0053
Example 14	2	78.5:8.0:4.5:8.7:0.2:0.0950	1200	1125	0.8	10	100	165	240	0.0005
							500		228	0.0010
Example 15	1	78.5:8.0:4.5:8.5:0.2:0.318	4000	1125	0.8	30	100	165	175	0.0086
							500		148	0.0090
Comparative Example 8	1	78.5:8.0:4.5:7.8:0.2:0.953	12000	1125	0.8	60	100	165	160	5.9030
							500		73	6.3310

After starting the feeding of raw materials, the inlet concentration (analysis value at (1) of Fig. 3) was stabilized within 50 hours, therefore, the operation was continued as it is. The reaction results calculated from the inlet concentration and the reaction gas concentration at the outlet (analysis value at (3) of Fig. 3) after 100 hours or 500 hours are shown in Table 5.

Examples 14 and 15 and Comparative Example 8

The reactions were performed in the same manner as in Example 13 except for changing the catalyst, the butene concentration and the temperature in the scrubber to the conditions shown in Table 5.

The reaction results are shown in Table 5.

Industrial Applicability

As described above, in the process for producing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, when the concentration of olefin having 3 or more carbon atoms in the raw materials is controlled to 10,000 ppm or less in terms of a molar ratio to the total of the olefin and ethylene or when the concentration of olefin equivalent in the raw materials is controlled to 50,000 ppm or less in terms of a molar ratio to the total of the olefin equivalent and ethylene, a stable operation can be continuously performed for a long period of time.

CLAIMS

1. A process for producing an ester, comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the  
5 concentration of olefin having 3 or more carbon atoms in the starting materials is 10,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

2. The process as claimed in claim 1, wherein the concentration of olefin having 3 or more carbon atoms in  
10 the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of the olefin and ethylene.

3. The process as claimed in claim 2, wherein the concentration of olefin having 3 or more carbon atoms in the starting materials is 1,000 ppm or less in terms of  
15 the molar ratio to the total of the olefin and ethylene.

4. The process as claimed in any one of claims 1 to 3, wherein the olefin having 3 or more carbon atoms comprises at least one compound selected from the group consisting of trans-2-butene, cis-2-butene and 1-butene.

5. A process for producing an ester, comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the concentration of olefin equivalent in the starting  
20 materials is 50,000 ppm or less in terms of the molar ratio to the total of the olefin equivalent and ethylene.  
25

6. The process as claimed in claim 5, wherein the concentration of olefin equivalent in the starting materials is 25,000 ppm or less in terms of the molar ratio to the total of the olefin equivalent and ethylene.

7. The process as claimed in claim 6, wherein the concentration of olefin equivalent in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of the olefin equivalent and the  
30 ethylene.

8. The process as claimed in any one of claims 5 to 7, wherein the olefin equivalent comprises at least one compound selected from the group consisting of  
35

saturated alcohols having 3 or more carbon atoms, esters of a carboxylic acid and a saturated alcohol having 3 or more carbon atoms, and saturated ethers having 5 or more carbon atoms.

5           9. A process for producing an ester, comprising reacting a carboxylic acid and ethylene in the presence of an acid catalyst in a vapor phase, wherein the sum of the concentration of olefin having 3 or more carbon atoms and one-fifth the concentration of olefin equivalent in  
10 the starting materials is 10,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

          10. The process as claimed in claim 9, wherein the sum of the concentration of olefin having 3 or more  
15 carbon atoms and one-fifth the concentration of olefin equivalent in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

          11. The process as claimed claim 10, wherein the sum of the concentration of olefin having 3 or more  
20 carbon atoms and one-fifth the concentration of olefin equivalent in the starting materials is 1,000 ppm or less in terms of the molar ratio to the total of the olefin and olefin equivalent and ethylene.

25           12. The process as claimed in any one of claims 9 to 11, wherein the olefin having 3 or more carbon atoms comprises at least one compound selected from the group consisting of trans-2-butene, cis-2-butene and 1-butene.

          13. The process as claimed in any one of claims 9  
30 to 12, wherein the olefin equivalent comprises at least one compound selected from the group consisting of saturated alcohols having 3 or more carbon atoms, esters of a carboxylic acid and a saturated alcohol having 3 or more carbon atoms, and saturated ethers having 5 or more  
35 carbon atoms.

          14. The process as claimed in any one of claims 1 to 13, wherein the carboxylic acid and ethylene is



reacted in the presence of water.

15. The process as claimed in any one of claims 1 to 14, wherein the carboxylic acid is at least one of lower aliphatic carboxylic acids having from 1 to 4 carbon atoms.

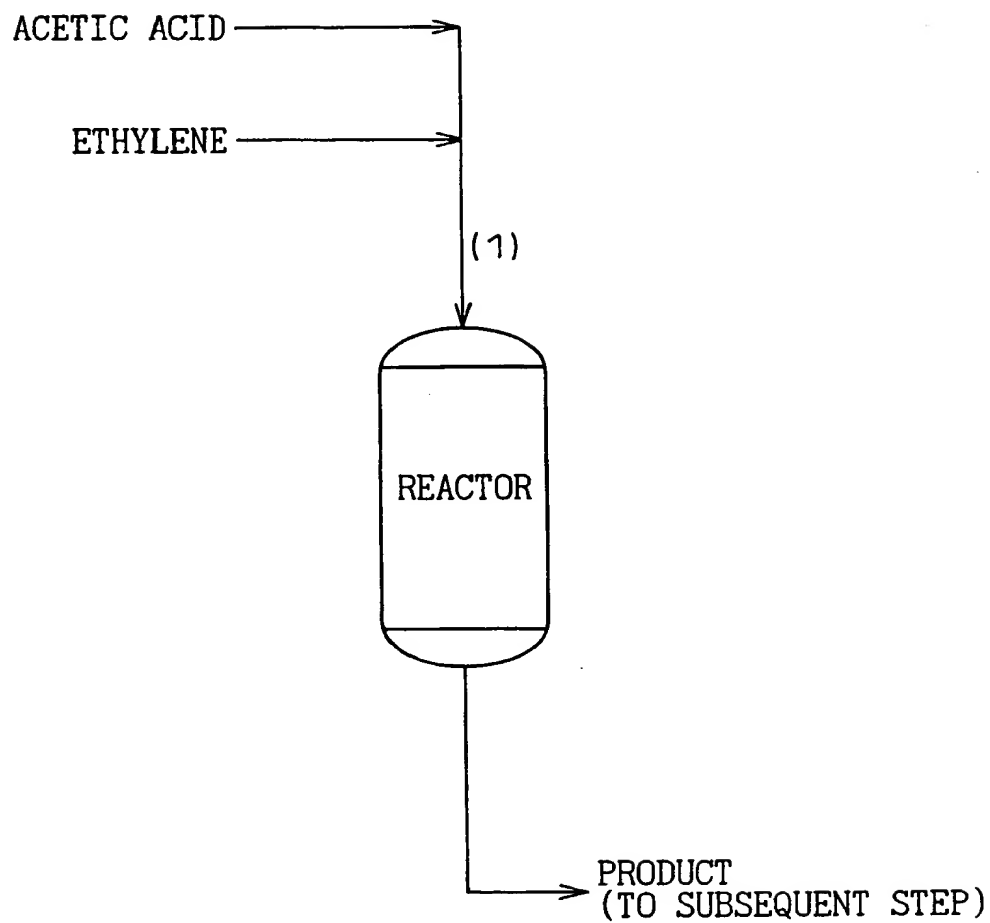
16. The process as claimed in any one of claims 1 to 15, wherein the acid catalyst comprises at least one compound selected from heteropolyacids and heteropolyacid salts.

17. The process as claimed in claim 16, wherein the heteropolyacid comprises at least one compound selected from the group consisting of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid, phosphovanadomolybdic acid, molybdotungstosilicic acid and molybdotungstophosphoric acid.

18. The process as claimed in claim 16, wherein the heteropolyacid salt comprises at least one compound selected from the group consisting of lithium, sodium, potassium, cesium, magnesium, barium, copper, gold, gallium and ammonium salts of heteropolyacids.

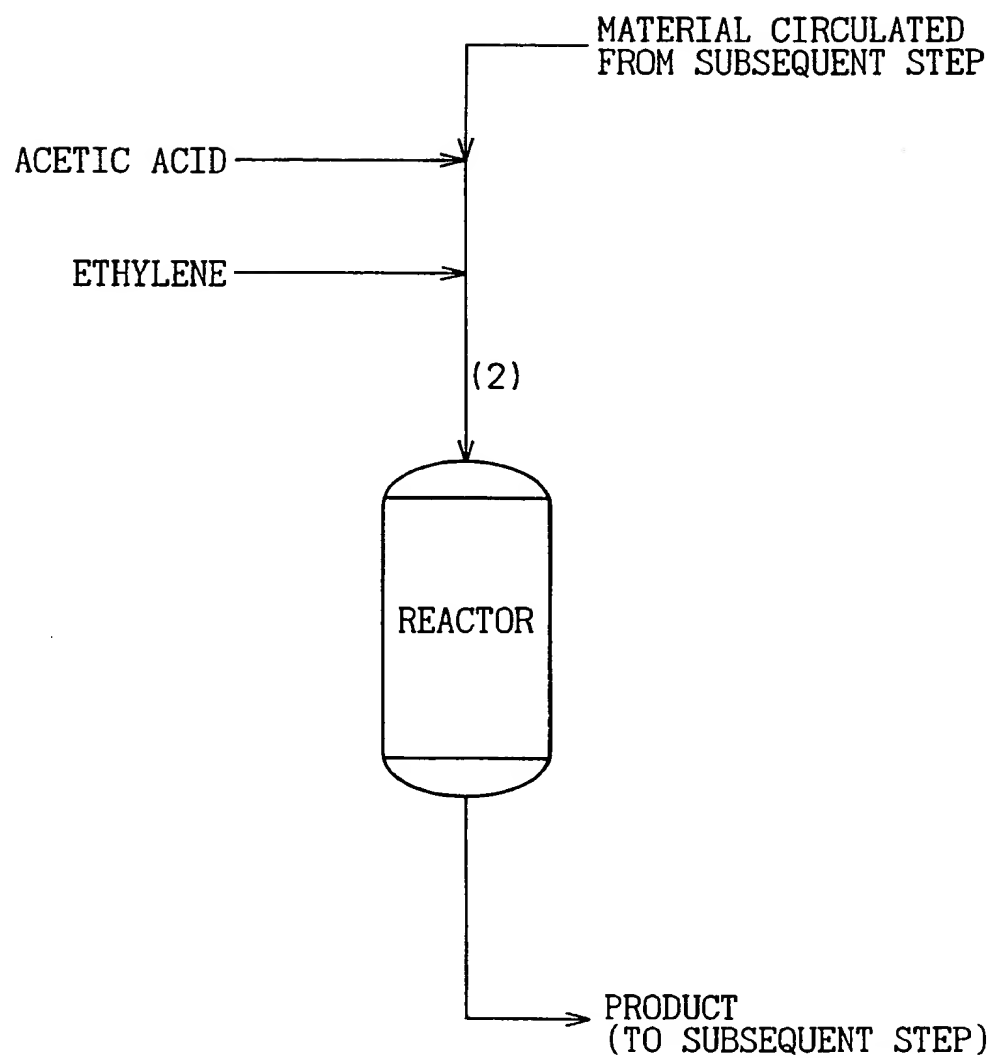
1/3

Fig. 1



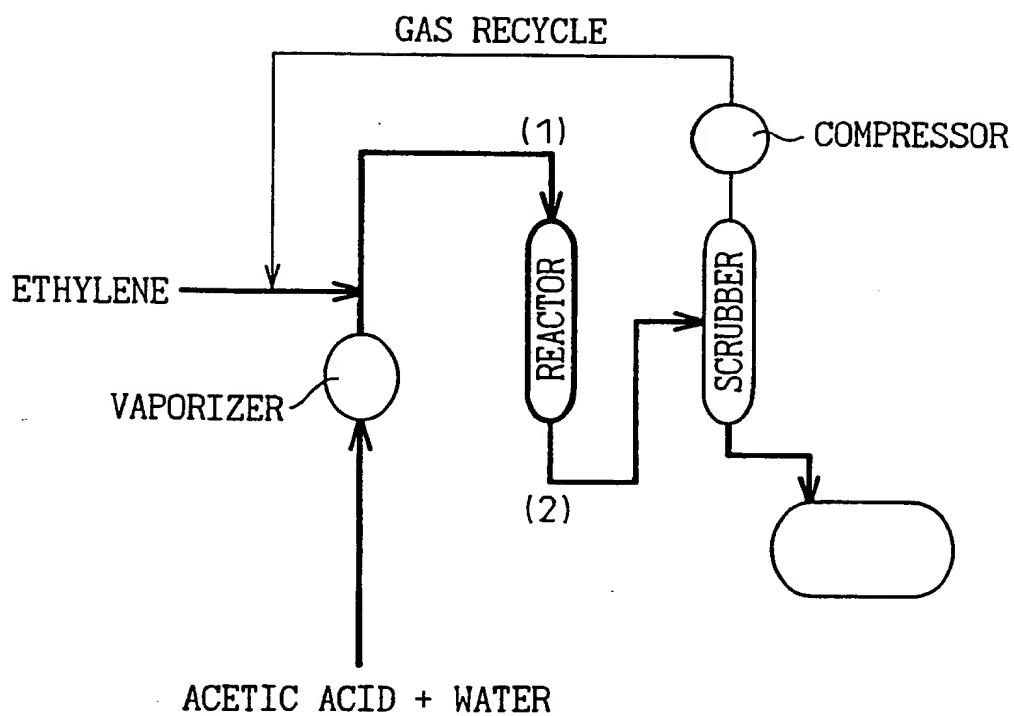
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Fig.2



3 / 3

Fig.3



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/07443

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/04 C07C69/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 562 139 A (SHOWA DENKO KABUSHIKI KAISHA) 29 September 1993 (1993-09-29) page 18 -page 19; claims	1
A	EP 0 757 027 A (BP CHEMICALS LIMITED) 5 February 1997 (1997-02-05) page 20 -page 22; claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Int l Application No

PCT/JP 00/07443

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